Report Number: InMat 2002-103

CBD SBIR Phase 1 Final Report: Improved Chemical Protective Gloves using Elastomeric Nanocomposites

Harris A. Goldberg and Carrie A. Feeney

Contract DAAD16-02-C-0041

November 14, 2002

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The Innovative Materials Company

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Exhibit A

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
14Nov02

3. REPORT TYPE AND DATES COVERED
Final Report 14May02 to 14Nov02

4. TITLE AND SUBTITLE
CBD SBIR Phase 1 Final Report: Improved Chemical Protective Gloves using Elastomeric Nanocomposites

5. FUNDING NUMBERS
Contract
DAAD16-02-C-0041

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
InMat LLC
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8. PERFROMING ORGANIZATION REPORT NUMBER
InMat 2002-103

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
US Army Robert Morris Acquisition, Natick Contracting Division
Kansas Street
Natick MA 01760-5011

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
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14. SUBJECT TERMS
SBIR Report, Gloves, Nanocomposites, Chemical Protection, Barrier Coating

15. NUMBER OF PAGES
15

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

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Table of Contents:

1) Abstract

Report developed under SBIR contract for topic CBD02-103. InMat has shown the feasibility of developing multilayer chemical protective gloves that provide the chemical protection of butyl rubber gloves but have improved flame and petroleum oil resistance. The enabling technology is based on InMat's aqueous nanocomposite elastomeric coatings that were specifically formulated for this application during Phase 1. Specifically, InMat demonstrated that 2-4 mils of its nanocomposite coatings offer the potential to provide the same 24 hours of protection currently available with 25-30 mil thick butyl rubber gloves. Neoprene nanocomposites were developed in Phase 1 and will be combined with Neoprene substrate in Phase 2 to provide the chemical warfare protection with improved adhesion to Neoprene, as well as improved resistance to flame and petroleum oils.

2) List of Figures

3) List of Tables

4) Preface: Description of Project & Objectives

In Phase I, we demonstrated the feasibility of InMat butyl nanocomposite technology as the basis for an improved multilayer glove compared to currently available butyl gloves, by combining InMat's aqueous suspensions (such as Neoprene). The resulting multilayer material will not use any solvent during glove production. The specific objectives in Phase I were:

- Develop aqueous nanocomposite coating formulations that can be coated on candidate substrate elastomers (such as Neoprene) chosen to provide complementary properties including resistance to petroleum based solvents and lubricants (POL) as well as for their flame resistance.
- Demonstrate that coated elastomeric substrates can provide an effective permeation barrier to chemical warfare agents.
- Demonstrate that nanocomposite coated substrates or multilayer structures can have better flame resistance than butyl rubber as measured by vertical flame testing.
- Show that coated substrates or multilayer structures can retain effectiveness as permeation barriers after exposure to petroleum based solvents and lubricants.

5) Acknowledgements

We gratefully acknowledge the assistance and input from Luc DeBecker and Bill Williams from Best Manufacturing Company. We also recognize the efforts of the InMat technical staff, specifically Michele Farrell, Doug Karim, Keisha Oree and Ray Carney.

6) Work Performed & Results

a) Baseline Chemical Warfare Agent protection and correlation with gas permeation

We have completed three separate rounds of testing of the effectiveness of our nanocomposite barrier coatings on reducing the permeation rate of chemical warfare agents. This testing was done by an independent outside laboratory, Geomet Technologies Inc.

Test 1: In this test we set out to demonstrate that our nanocomposite barrier coatings, already in use as a gas barrier, can be effective as a barrier to chemical warfare agents. The results are shown in Figure 1. The primary conclusion from this test is that two layers (each ~1 mil thick) can provide 2-3 times the protection against mustard gas as a 9 mil butyl rubber glove.

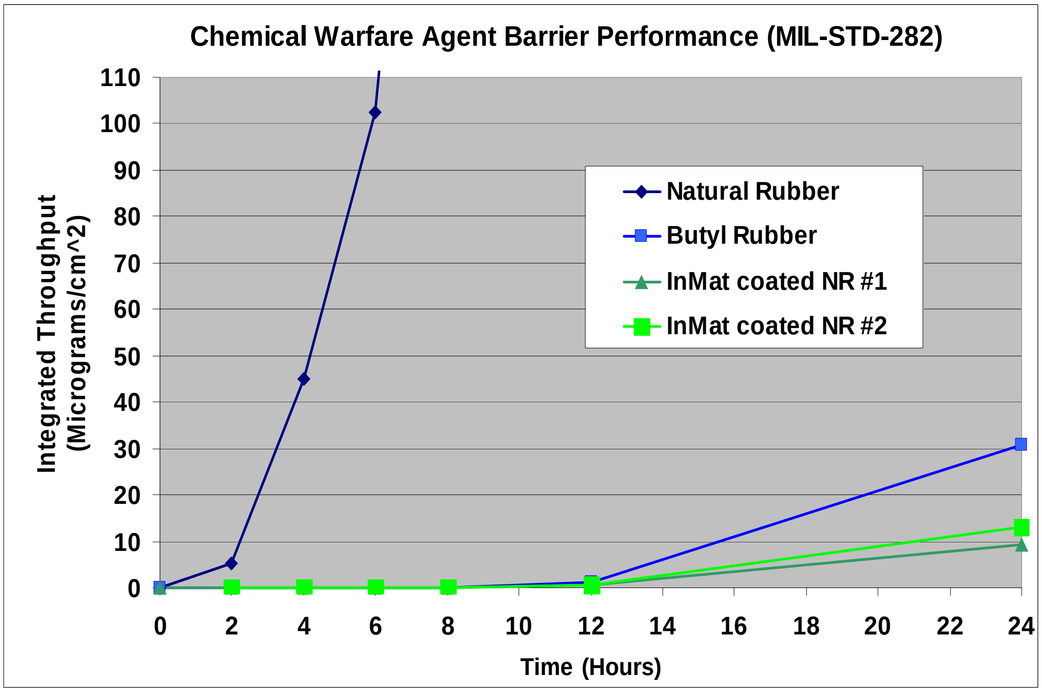

Figure 1: InMat coatings on natural rubber provide better protection against mustard gas than a butyl rubber glove.

Test 2: In this test we set out to compare our commercial nanocomposite coatings to a new developmental formulation that has a much lower (factor of about 2) gas permeability. The objective was to start to understand the correlation between gas permeability and protection from chemical warfare agents. We also did our first testing using nerve gas at this time. The samples were coated on polypropylene film (0.8 mil or 20 microns) since this is the same substrate we use for gas permeation testing, and we find that it has very consistent properties. The results are shown in Tables 1 and 2 below.

Table 1. Chemical Warfare Testing of InMat Samples – Mustard Gas[1]

Notebook#	OTR[2]	Breaktime[3]	Amount @ 24 hrs[4]	Description
20021-08-1	3750	>12 hr	10.0	0.02 mm uncoated PP film
20021-08-3	55	>24 hr	3.2	0.048 mm AD2000 coated on both sides PP
20021-08-4	47	>24 hr	3.0	0.056 mm AD2000 coated on both sides PP
20021-08-7	34	>24 hr	2.8	0.035 mm AD3000 coated on both sides PP
20021-08-8	29	>12 hr	4.4	0.042 mm AD3000 coated on both sides PP

Notes:

1. Mustard gas measurement MIL-STD-282, method 209.1 done by Geomet Technologies.
2. OTR is oxygen transmission rate reported in units of cc/m2 day atm @ 23C, 0% RH.
3. Breaktime for HD (mustard gas) is 4.0 ug/cm2 for blistering (desication) according to report ECBC-TR, "Swatch Test Results of Commercial Chemical Protective Gloves to Challenge by Chemical Warfare Agents: Summary Report", by Robert S. Lindsay, February 2001. Break time for rash is 2.0 ug/cm2 (erythema) according to the same report. The number reported here is for blistering to occur. [1,2]
4. Reported in units of ug/cm2.

Table 2. Chemical Warfare Testing of InMat Samples – Nerve Gas[1]

Notebook #	OTR[2]	Breaktime[3]	Amount @ 24 hrs[4]	Description
20021-08-2	3750	>24 hr	1.306	0.02 mm uncoated PP film
20021-08-5	59	>24 hr	0.0046	0.046 mm AD2000 coated on both sides PP
20021-08-6	52	>24 hr	0.00034	0.051 mm AD2000 coated on both sides PP
20021-08-9	31	>24 hr	0.001	0.039 mm AD3000 coated on both sides PP
20021-08-10	27	>24 hr	0.001	0.044 mm AD3000 coated on both sides PP

Notes:

1. Nerve gas measurement MIL-STD-282, method 208.1 done by Geomet Technologies.
2. OTR is oxygen transmission rate reported in units of cc/m2 day atm @ 23C, 0% RH.
3. Nerve gas threshold is a systemic response (not local like mustard gas) according to report ECBC-TR, "Swatch Test Results of Commercial Chemical Protective Gloves to Challenge by Chemical Warfare Agents: Summary Report", by Robert S. Lindsay, February 2001. Threshold for incapacitation is 9.5 ug/cm2 and for fatality is 17.8 ug/cm2. These thresholds are also from the above report. [1,2]
4. Reported in units of ug/cm2.

It is important to note that there was significant variability in the amount that comes through after 24 hours. We further note that the AD 3000 sample was not a factor of two less permeable to oxygen because the coating was thinner. The AD 2000 had about 50 microns for the total barrier coating thickness (two layers) while the AD 3000 had about 40 microns total coating thickness.

The conclusions from this test are:

- InMat barrier coatings provide more than enough protection against nerve gas. Mustard gas is the more difficult material to protect against, and future testing will focus there.
- There is not a simple correlation between oxygen permeation rate and chemical warfare penetration rate. We suspect that the details of thickness, choice of substrate, and specific interactions will also play a role. We can and will continue to use gas permeability as an important screening tool and a qualitative indicator that a good barrier coating has been applied.
- About 2 mils of InMat's nanocomposite barrier coating are close to providing 24 hours of protection even when used on a very thin substrate. To insure full protection (< 4 ug/cm2) from mustard gas better barriers, more layers, or thicker layers will be required. Regardless, the total thickness required will still be much less than the 15-30 mils currently used in butyl rubber gloves.

b) Baseline Flame Resistance Testing

The flame testing chamber was designed and built to test flat sheet with coating. The entire chamber can be closed to control flames. In addition, the flame height is set using a valve with the bottle exterior to the chamber.

The type of testing is also modified to test a flat sheet with a coating instead of placing the sample vertical. This will better mimic working conditions with a glove. We will measure the time to ignition.

Using this flame chamber, uncoated glove substrates were tested for time to ignition to determine a baseline requirement. The results are listed in Table 3 below.

Table 3. Flame Testing of Uncoated Substrates

NB#	Sample	Flame Distance (inches)	Ignition Time (seconds)
20021-20-8	14 mil Neoprene	0.25	9
20021-20-10	14 mil Neoprene	0.75	18
20021-21-1	25 mil butyl	0.25	18
20021-21-3	25 mil butyl	0.75	25
20021-21-4	14 mil butyl	0.25	12
20021-21-6	14 mil butyl	0.75	33

c) Baseline Petroleum Oil Resistance Testing

InMat used the following procedure to test petroleum oil resistance: Prepared 3"x3" samples soaked in Super Duty Motor Oil SAE 10, evaluated for weight uptake after specified time intervals. The data are listed below in Table 4.

Table 4. Weight Update in Petroleum Oil

	Weight Uptake (grams)			
Sample	30 minutes	1 hours	3 hours	24 hours
Butyl	0.28	0.41	0.43	1.02
Neoprene	0.17	0.19	0.27	0.66

This test was refined to mimic glove conditions based on results in Table 4. Samples 2”x2” were prepared and exposed to the same POL for 30 minutes, the residual oil wiped off and the sample tested for OTR. The results are listed in Table 5 for uncoated substrates.

Table 5. POL Testing on Uncoated Substrates: Increase in OTR[1].

Sample	OTR Initial	OTR 30 min	% Increase	OTR 24 hrs	% Increase
14 mil Neoprene	631	676	7.1	728	15
14 mil butyl	167	183	9.6	249	49
25 mil butyl	127	135	6.3	162	20

Note:
1. OTR is oxygen transmission rate reported in units of cc/m2 day atm at 23C, 0% RH.

The initial OTR values are consistent with those reported in the literature [3,4]. The OTR values can vary substantially depending upon the details of the additive package of the base rubber. This table clearly shows that the Neoprene substrate is more resistant to POL exposure than butyl rubber. Therefore, this will be explored further.

d) Modified Formulations for Improved Properties

The Air D-Fense 2000 and 3000 formulations tested to date are made from a butyl matrix. This matrix is known to be damaged by both flame and POL (see baseline testing above) [5]. Therefore, modifications to the butyl matrix were done to improve the properties of the film. Neoprene latex was substituted for the butyl matrix in a variety of concentrations to determine the improvements in flame and POL properties. Formulations containing 50%, 80%, 95% and 100% Neoprene in the matrix were made into Air D-Fense 3000 and tested using standard InMat QC.

It is important to monitor the reduction in permeability so that optimum dispersion of the filler is maintained while changing the polymer matrix. The interaction of the polymer and the filler is extremely sensitive and the formulation may need modifications if the dispersion suffers from the change in polymer. The resulting permeability and reduction in permeability for each modified formulation is listed in Table 6. Permeability is reported, not OTR, because then the substrate and thickness contributions can be taken out of the value and the type of coating compared directly. Permeability is reported based on the assumption that the coating thickness is 1 mm thick.

Table 6. Modified Air D-Fense ™ 3000: ChemWall ™ Formulation Oxygen Permeability[1]

Formulation	Neoprene %	Unfilled Permeability	Filled Permeability	Permeability Reduction[2]
AD3000	0	90	0.85	106
CW NB3050	50	181	2.1	86
CW NB3080	80	239	1.4	170
CW NB3095	95	263	1.35	195
CW N3000	100	272	1.4	194

Notes:
1. Permeability is measured in units of cc mm/m2 day atm @ 23C, 0% RH on polypropylene films.

2. Permeability reduction is times permeability reduced from unfilled permeability.

i) Flame Testing on Modified Formulations

The new formulations were coated onto 14 mil Neoprene glove substrate and tested using the flame testing chamber built and designed by InMat. The data are listed below in Table 7.

Table 7. Flame Testing of Modified Formulations on Neoprene Glove[1]

NB#	Sample[2]	Ignition Time (seconds)
20021-16-1	AD3000	4
20021-14-5	CW NB3050	5
20021-16-4	CW NB 3080	7
20021-13-9	CW NB 3095	7
20021-17-8	CW N3000	8
20021-18-9	Uncoated Neoprene	8
20021-18-7	Uncoated butyl	7

Notes:
1. Modified formulations coated onto 14 mil Neoprene Glove substrate.
2. Sample designation denotes an increasing amount of Neoprene content in the matrix. AD3000 contains 100% butyl whereas CW N3000 contains 100% Neoprene.
3. OTR is oxygen transmission rate reported in units of cc/m2 day atm @ 23C, 0% RH.

In this flame testing method, the flame was actually on the sample. In the previously reported uncoated substrates, the flame was removed from the sample. As the Neoprene content of the matrix is increased, the ignition time is also increased. Therefore, if the coating was on the outside of the glove, or if the flame penetrated through the outer glove layer into the barrier layer, the Neoprene content of the barrier layer would add flame resistance to the overall glove.

ii) POL Testing on the Modified Formulations

Using the same method described for the baseline POL testing on glove materials, the modified formulations were tested for OTR before and after exposure to POL (30 minutes and 24 hr intervals). The data for the coated substrates are listed below in Table 8.

Table 8. POL Testing on Modified Formulations coated onto Neoprene Substrate[1].

Sample[2]	OTR[3] Initial	OTR[3] 30 min	% Increase[4]	OTR[3] 24 hours	% Increase[4]
AD3000	51.5	275.1	534	Fell apart	N/a
CW NB3050	67.7	267.5	395	Mushy	N/a
CW NB3080	56.9	126	221	275	483
CW NB3095	54.4	71.5	31	151.6	278
CW N3000	79.3	103.8	31	128.6	62

Notes:
1. Modified formulations coated onto 14 mil Neoprene Glove substrate.
2. Sample designation denotes an increasing amount of Neoprene content in the matrix. AD3000 contains 100% butyl whereas CW N3000 contains 100% Neoprene. All coatings are between 13-18 microns.

3. OTR is oxygen transmission rate reported in units of cc/m2 day atm @ 23C, 0% RH.
4. % Increase is calculated from the initial OTR.

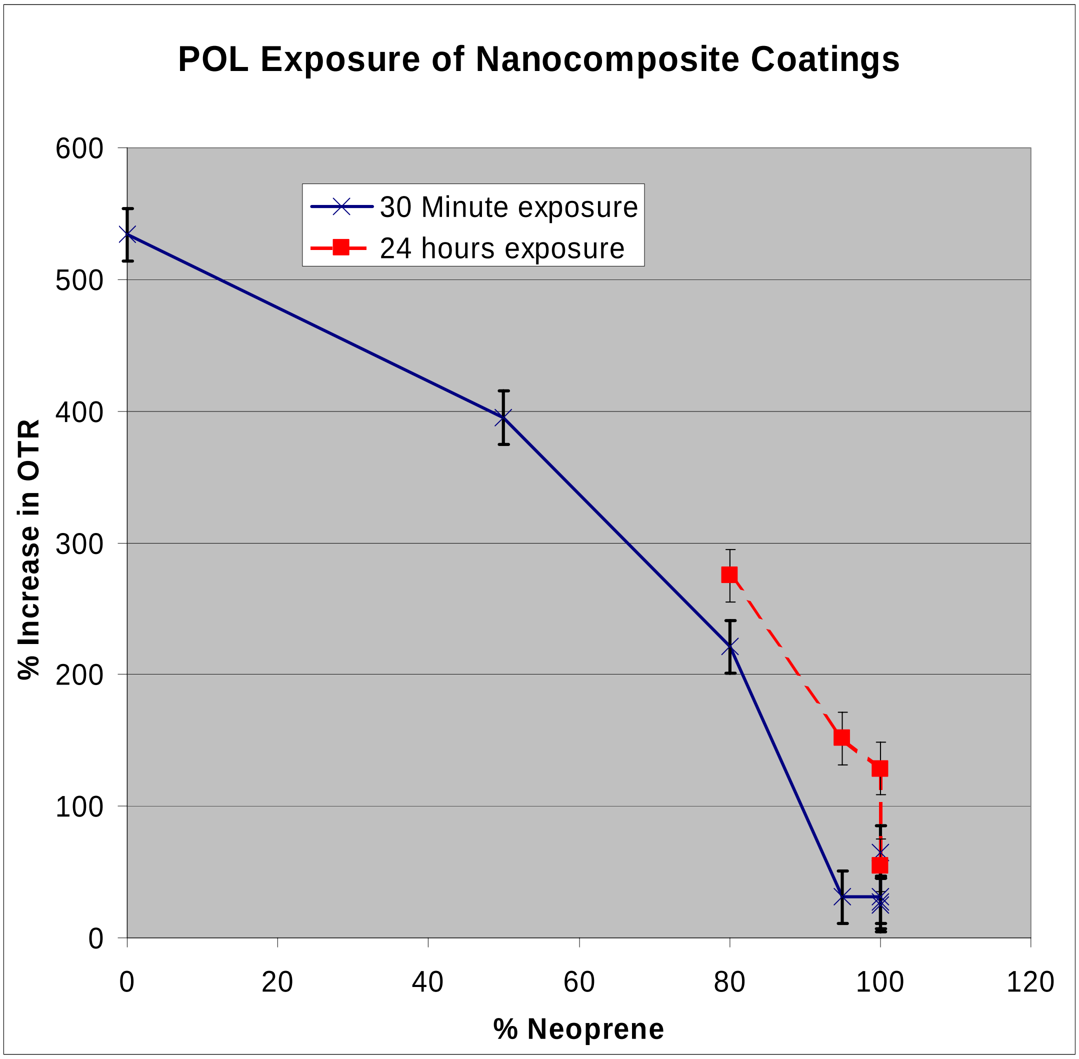

Figure 2. Neoprene nanocomposites have much lower changes in oxygen permeability when exposed to petroleum oil.

As the Neoprene content of the matrix is increased, the % increase upon exposure to POL is reduced. Therefore, if the coating was on the outside of the glove, or if the POL penetrated through the outer glove layer into the barrier layer, the Neoprene content of the barrier layer would add POL resistance to the overall glove.

POL testing on neoprene samples was done to determine whether the neoprene nanocomposite was slowing the penetration of the POL through the sample. OTR after exposure (30 minutes) to POL was measured and the initial OTR was calculated based on the permeability and coating thickness. The samples and results are listed in Table 10 below. Additionally, POL testing on Neoprene samples was done repeatedly to determine the reproducibility of this type of testing. Hydraulic oil was also used. These data are also reported in Table 9.

Table 9. POL Testing on Neoprene Substrate[1] Coated with ChemWall™ N3000 – Multiple Runs with motor oil and hydraulic oil- 30 minutes

Sample	Motor Oil Testing (% Increase in OTR)					Hydraulic Oil (% Inc OTR)
	Run 1	Run 2a	Run 2b	Run 3a	Run 3b	Run 1
Uncoated	15	165	62	11		243
Single Coated Side	62	74	55	27	25	29
Single Uncoated Side		4	9	0	0	16
Double coated		0	12	9	22	0

Note: 1) Neoprene substrate is commercial glove, 18 mil thick.

The data from Table 9 are shown graphically in Figure 3 below. It is clear that the % increase in OTR due to exposure to petroleum oil or hydraulic oil on the uncoated side or the double coated sample of neoprene substrate is consistently lower than the % increase in OTR of the coated side of Neoprene with the same exposure. In addition, the uncoated Neoprene sample is not consistent over 5 runs.

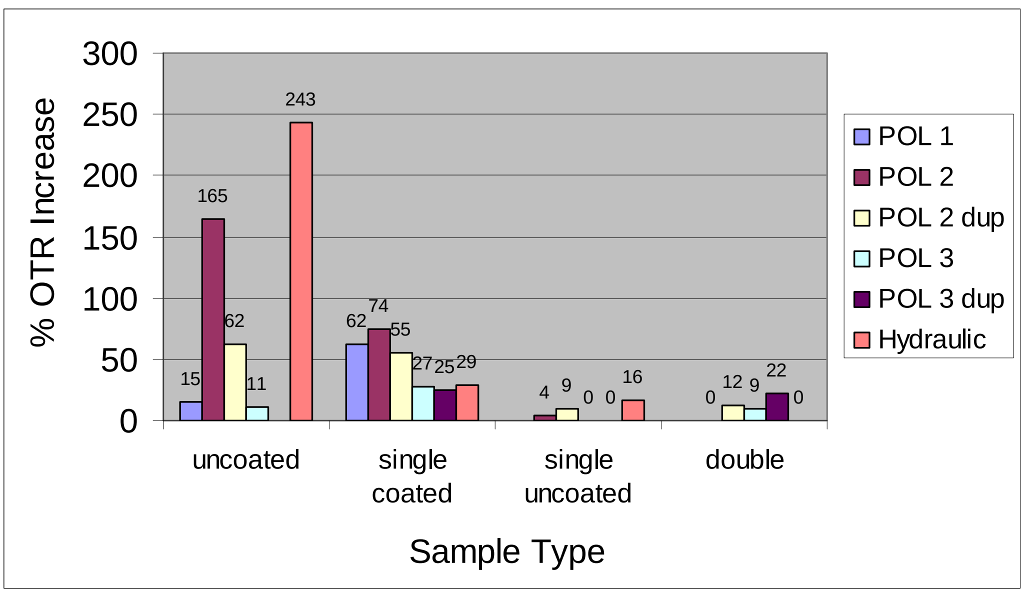

Figure 3. POL results of multiple runs of ChemWall™ N3000 on Neoprene glove substrate and uncoated Neoprene glove substrate, 18 mil thick.

iii) <u>Chemical Warfare Agent Testing of Modified Formulations (Neoprene Nanocomposites)</u>

Nine samples were submitted to Geomet Technologies for mustard gas testing (Method 209.1: HD Resistance of Impermeable Materials). The samples are listed below in Table 10. The substrate for all the samples was Neoprene glove material, 18 mil thickness. The new Neoprene nanocomposite (ChemWall™ N3000) was evaluated by itself as well as with the butyl nanocomposites (Air D-Fense™ coatings). In this testing, we tried to answer several questions at once. They were:

- How do our coatings perform on a Neoprene substrate?

- How do the new Neoprene based nanocomposites perform as chemical warfare agent barriers?
- How does the protection improve as the number of barrier layers increase?

Table 10. Geomet Samples for Mustard Gas Testing

NB #	Sample	Description
20021-26-1	Uncoated Neoprene	0.46 mm Neoprene glove material (18 mil)
20021-26-2	AD2000 Double	Coated on both sides: 62.7 micron total
20021-26-3	AD3000 Double	Coated on both sides: 40.8 micron total
20021-26-4	CW N3000 Single	Coated on one side: 13.2 micron
20021-26-5	AD2000 Single	Coated on one side: 23.8 micron
20021-26-6	AD3000 Single	Coated on one side: 16.3 micron
20021-26-7	CW N3000 Double	Coated on both sides: 36.9 micron total
20021-26-8	AD2000/CW N3000 combo	30.0 microns AD2000 on one side 13.7 microns CW N300 on other side
20021-26-9	AD3000/CW N3000 combo	16.4 microns AD3000 on one side 14.7 microns CW N3000 on other side

The results from the chemical warfare testing using mustard gas are presented in Table 11 below.

Table 11. Chemical Warfare Agent Testing on Neoprene Nanocomposites (ug/m2)

NB #	Sample	Sampling Intervals (Hours from Start)						Cum
		0-2	2-4	4-6	6-8	8-12	12-24	
20021-26-1	Uncoated Neoprene	80.4	498.4	583.8	526.8	987.8	1883.4	4560.6
20021-26-2	AD2000 Double	0.8	0.8	1.0	1.6	4.0	28.8	37.0
20021-26-3	AD3000 Double	0.8	1.0	25.8	65.4	93.6	82.8	269.4
20021-26-4	CW N3000 Single	0.8	118.0	319.8	283.0	410.6	1163.6	2295.8
20021-26-5	AD2000 Single	0.8	28.6	94.0	217.4	624.4	2171.4	3136.6
20021-26-6	AD3000 Single	0.8	113.6	424.8	476.2	905.6	2440.4	4361.4
20021-26-7	CW N3000 Double	0.8	5.8	342.0	228.0	459.8	1261.6	2298.0
20021-26-8	AD2000/CW N3000combo	0.8	0.6	21.2	31.6	68.0	93.6	215.8
20021-26-9	AD3000/CW N3000combo	0.4	2.2	39.8	95.6	94.0	208.6	440.6
For Comparison to Previous Data:								
38908-49-3	Uncoated NR 28 mil	5.1	40.0	57.3	159.4	300.9	804.4	1367.1
38908-49-4	AD2000 coated NR	ND	ND	ND	ND	0.5	8.8	9.3
20021-08-1	Uncoated PP 0.8 mil	0.4	0.6	0.8	0.8	1.8	5.6	10.0
20021-08-3	AD2000 coated PP	ND	0.2	0.2	0.2	0.6	2.0	3.2

The data listed in the top section of Table 11 are all done on Neoprene glove substrate, 18 mil thick. The data listed in the bottom section of Table 11 are for comparison.

According to a report by Robert S. Lindsay, "Swatch Test Results of Commercial Chemical Protective Gloves to Challenge by Chemical Warfare Agents: Summary Report" dated February 2001 [1,2], natural rubber should be at least 10 times more permeable to mustard gas than Neoprene rubber. This is not consistent with the results that were reported from Geomet Technologies. According to their results, the natural rubber is about 3 times better barrier than Neoprene rubber. We questioned Geomet on this result and their response was that "a thin spot in the Neoprene" could account for this difference.

Another discrepancy was the barrier performance of Air D-Fense 2000, our best chemical barrier to date. On natural rubber, the breakthrough occurred between 12-24 hours. On polypropylene, the breakthrough occurred >24 hours. However, on Neoprene rubber, breakthrough occurred between 2-4 hours.

If we look at the penetration rate of HD we also find that the data is inconsistent. The coated polypropylene has a penetration rate of 0.1-0.2 ug/cm2-hour. The uncoated polypropylene has a penetration rate of 3-4 times that. We can therefore conclude that the penetration rate of mustard gas through 2 mils of Air D-Fense 2000 should be less than 0.27 ug/cm2-hour. The results on natural rubber are a factor of 2-3 higher than this. The results on Neoprene are a factor of 10 higher. These points to an interaction between the mustard gas and the substrate which affects the barrier provided by our coating. The most likely explanation is swelling of the substrate that leads to damage an/or delamination of the nanocomposite coating. We cannot examine the samples after testing by Geomet, making a determination as to the mechanism causing these problems difficult. In Phase 2 we will work with Best Manufacturing to set up simulant testing., which should help resolve these issues.

To summarize, the results were surprising and inconsistent with our earlier tests. The mustard gas penetration of the uncoated Neoprene was almost a hundred times what we expected from published results [1,2]. Although some of our coated samples showed large improvements, all samples in this test were more permeable than expected. At this time we do not know the reason and additional testing in phase 1 option and phase 2 will be required to understand what happened. Two likely scenarios have to do with the details of the Neoprene substrate chosen, and the details and reproducibility of the tests. Based on the problems encountered in this test, some of the key issues that will be addressed include:

- Differences in the properties of different Neoprene formulations with respect to its interaction with mustard gas.
- The effect of curing, including the type and amount on Neoprene properties.
- The effect of swelling or other changes in the substrate on the barrier properties of InMat's nanocomposite coatings.

e) <u>Glove Partner Initial Work</u>

Best Manufacturing, our proposed sub-contractor for Phase 2, has produced several multilayer glove samples at their laboratory in Menlo, GA. They have evaluated some of these samples for breakthrough time for commonly used solvents. Table 12 compares results for gloves that used 1 mil of Air D-Fense™ 2000 (100% butyl nanocomposite) on 3 mils of Neoprene. The inside layer was 2 mils of nitrile. A 1-2 micron polyurethane slip layer was put over the nitrile layer. The breakthrough times for this glove (total thickness 6 mils) is compared with butyl and Neoprene gloves that are much thicker [6]. Figure 4 shows a picture of one of the gloves tested for solvent breakthrough time.

Table 12. Solvent Breakthrough times (minutes): Thin multilayer glove protects against solvents better than a much thicker Neoprene glove.

Solvent	Neoprene Glove #723 (14 mil) #6780 (30 mil)	Multilayer Glove: 6 mil Neoprene 3 mil AD2000 1 mil Nitrile 2 mil	Butyl Glove 14 mil
Acetone	15 35	41	139
Acetonitrile	36 65	137	>480
Methanol	55 226	236	>480

Figure 4. This glove, produced in Best Manufacturing's research center, has a Neoprene outside layer, InMat's Air D-Fense™ 2000R layer, and an inside layer of nitrile rubber. The pink color on the inside is due to the Air D-Fense™ 2000R, still visible through the nitrile rubber layer.

In addition to solvent testing, the gloves were evaluated using oxygen transmission rate. The gloves were cut into samples by section and evaluated for consistent OTR and calculated permeability. The OTR consistency would evaluate the overall dipping performance and the calculated permeability would evaluate how well the formulation was wetting on the Neoprene substrate. The results are listed in Table 13.

Table 13. Multilayer Glove Oxygen Transmission Rate Results (cc/m2 day atm)

Glove	Front of Glove			Back of Glove		
	Top/ fingers	Middle/ palm	Bottom/ wrist	Top/ fingers	Middle/ palm	Bottom/ wrist
1	98	91	185	86	83	155
2		93			85	
3		86			87	
4		93			106	

Glove Layers (Outside to Inside) Neoprene, Air D-Fense™ 2000R, Nitrile, Polyurethane

Based on the permeability of each layer and a best guess at thickness of the Air D-Fense™ 2000R layer, the permeability of the barrier coating can be calculated. The quoted Q.C. value for AD2000R on polypropylene is 2.5-3.5 cc mm/m2 day atm. The OTR values reported in Table 13 correspond to an approximate permeability of 2.6 cc mm/m2 day atm. The only part of the glove in question is bottom of the glove near the wrist. The coating may be thinner at this area. However, this is an excellent demonstration of the feasibility of using nanocomposite barrier coatings to provide an overall barrier to the glove using standard glove dipping technology.

In addition to solvent and OTR testing, the multilayer glove prototypes made by Best Manufacturing which have a layer of Air D-Fense™ 2000R between Neoprene and nitrile (total thickness 6 mil) were tested for POL resistance. Both sides of the glove were exposed to 30 minutes of motor oil and then the OTR measured. The results are listed in Table 14 below.

Table 14. POL Testing of Multilayer Nanocomposite Glove (% Increase OTR)

Layer with Oil	**% Increase OTR**
Neoprene Side	19
Nitrile Side	15

Glove Layers (Outside to Inside) Neoprene, Air D-Fense™ 2000R, Nitrile, Polyurethane

This is an encouraging result. However, more work comparing Best's Neoprene to that used in earlier tests (and cut from Ansell gloves) is needed to draw any firm conclusions.

f) Neoprene Nanocomposite (Modified Formulations) Scale-up

ChemWall™ N3000, Neoprene nanocomposite, and ChemWall™ NB3080, Neoprene/butyl nanocomposite blend, were scaled-up to 1 gallon batch sizes. This is the minimum for the glove dipping process. These formulations were shipped to Best Manufacturing for evaluation and feedback on the ease of use for the dipping process. Best Manufacturing did not use the formulations for about 6 weeks. After sitting, the formulations were unstable. Upon shear from mixing to de-aerate, both formulations agglomerated. They did not age well. The formulations need to be modified to improve stability and aging.

g) Options for Additional Neoprene Nanocomposite Modifications

i) Commercially Available Neoprene Latex

In preparation for phase 1 option and phase 2 and in consideration of the aging and stability issues, more information on commercially available Neoprene latex was accumulated. This information will provide options and direction for improvements in the current ChemWall formulations. The information is compiled in Table 15 below and points out the pros and cons of each latex. All the modifications to date have been done with Neoprene 750, the general purpose glove dipping latex. Interesting properties are highlighted for further study.

Table 15. Commercially available Neoprene Latex

Latex	Pros	Cons
Aquastick 2901: Polychloroprene homopolymer	• High modulus • Low temperature	• Anionic • Potassium salt • PH 12.5
Aquastick 1120: Chloroprene copolymer with carboxyl functionality	• **Resistance to prolonged mixing and destablilizers** • **Non-ionic** • **PVOH emulsifying agent** • **PH 7** • Crosslink with zinc oxide	• Additives that react with PVOH will cause thickening and/or flocculation of latex but no coagulation
Neoprene 400: Chloroprene copolymer with 2,3-dichloro-1,3-butadiene	• **Large amount of chlorine** • **Best flame resistance** • Ozone barrier • Weather barrier • **Abrasion resistance** • Low surface tack	• Anionic • Potassium salt • PH 12.5 • Crystallization reversible
Neoprene 842A: Polychloroprene homopolymer	• Medium modulus	• Anionic • Sodium salt • PH >12
Neoprene 622: Polychloroprene homopolymer	• Medium modulus • **High solids with low viscosity** • **No creaming agent**	• Anionic • Potassium salt • PH >12 • Easily foams
Neoprene 671A: Polychloroprene homopolymer	• High modulus • High solids with low viscosity • **Wet gel strength**	• Anionic • Potassium salt • PH >12
Neoprene 571: Chloroprene copolymer with sulfur	• High modulus • High tensile strength • **Cured films have good hot oil resistance**	• Anionic • Potassium salt • PH >12
Neoprene 750:	• General purpose Neoprene	• Anionic

Chloroprene copolymer with 2,3-dichloro-1,3-butadiene	• Stable shelf life • Stable to heat aging • Natural rubber characteristics • Excellent crystallization • Good wet gel strength	• Potassium salt • PH >12

ii) Cure Packages for Neoprene

A number of cure packages were recommended for further study. These cure packages differ depending upon what characteristics of the final film is required, such as heat resistance, water resistance, low or high temperature stability, etc. They are commercially available from American Cyanamid and Vanderbilt and other specialty formulators.

iii) Formulation Process Modifications

Discussions with Neoprene experts have helped identify several processing methods and additives which should improve the stability and performance of Neoprene. Key factors that will be studied in phase 2 include:

- relative humidity
- additives that stabilize the Neoprene at lower pH
- amounts of additives and order of addition

7) Summary: Technical Feasibility

In phase 1, InMat has demonstrated the feasibility of combining its elastomeric nanocomposite coating technology [7-10] with existing glove materials produced entirely from aqueous dispersions. The initial demonstration was a 6 mil multi-layered glove with InMat's butyl nanocomposite on a Neoprene glove with a layer of nitrile rubber on the inside. The thin, multi-layered glove was evaluated for solvent resistance. This 6 mil multi-layered glove, much thinner than commercial protective gloves, provided an intermediate level of protection between Neoprene and butyl rubber.

Earlier measurements showed that the butyl nanocomposite provided barrier performance capable of 12-24 hour protection from chemical warfare agents with only 2 mils of thickness instead of the 30 mils typically used. This meant that a thinner glove could be produced, and that the bulk of the glove could be made from Neoprene. Neoprene gloves are easily produced from aqueous dispersions, and are known to have superior flame and petroleum oil resistance as compared to butyl rubber gloves [5]. Butyl rubber gloves are used only because of their superior ability to protect against chemical warfare agents and other hazardous materials [11]. Although the chemical warfare data were inconsistent on Neoprene, a thinner glove providing adequate protection is still feasible. These data were also inconsistent with data reported in the literature [1,2]. Both of these inconsistencies just highlight the need to further understand the details of the Neoprene substrate.

The third important accomplishment in phase 1 was the development of new nanocomposites based on Neoprene and Neoprene – Butyl blends. These formulations lead to coatings with even larger reductions in gas permeation relative to the unfilled polymer than the earlier butyl rubber based nanocomposites. This means that the dispersion is better, and that they should provide the same level of protection as butyl based nanocomposites.

Preliminary evaluation of the change in gas barrier properties showed that Neoprene based nanocomposites on the inside of a Neoprene glove could be exposed to petroleum oil for 24 hours or more without any change in gas barrier properties. In addition, our glove manufacturing partner, Best Manufacturing, has reported that the use of Neoprene in our nanocomposite formulations improves the adhesion to their Neoprene glove material.

InMat has demonstrated its capability to develop aqueous coating formulations that provide large improvements in the barrier properties of polymers. By applying that capability to elastomers that are useful in chemical protective gloves, new gloves which provide 24 hour protection against chemical warfare agents while providing improved resistance to flames and petroleum oils are feasible and can be developed. The new barrier coatings developed in this program will also be valuable in other applications including:

- Commercial chemical protective gloves
- Chemical protective hoods and face masks
- Chemical protective suits
- Tent materials
- Rubber hoses for fuel lines
- Inflatable boats

8) References

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